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## SINTERED CERAMIC MATERIALS PRODUCED FROM HYDROMICA CLAYS

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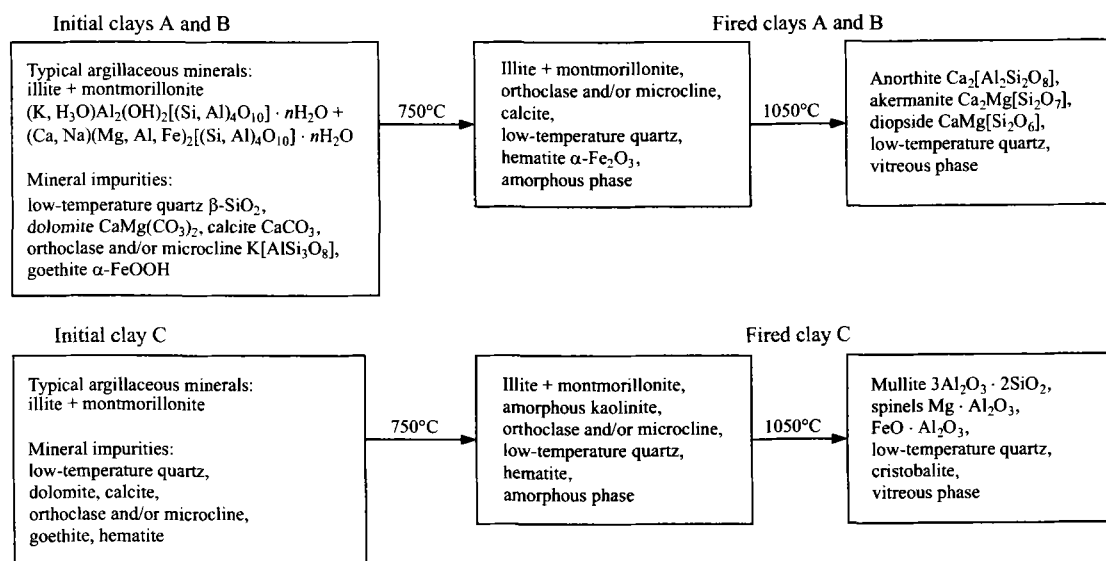
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Results of studying the process of sintering of two similar-type ceramic mixtures made of three varieties of low-melting illite-containing clays with additives of nepheline sienite and synthetic pseudowollastonite are described. The expediency of using several varieties of similar-type clays with different mineralogical and granulometric compositions to expand the sintering interval is shown.

The process of ceramic-material production and the properties of the resulting product are closely related to the

behavior of the material mixture in firing. This technological cycle acquires special importance in the production of dense ceramic articles (known as “stone goods”) from low-melting (melting point  $\geq 1080^\circ\text{C}$ ) hydromica (illite-containing) clays.

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**Scheme 1.** Change in the phase composition of the clays under heating.

**TABLE 1**

Material	Mass content, %								
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	calcination loss
Clay:									
A	49.89	17.21	7.20	0.81	5.88	3.98	0.54	3.96	10.53
B	46.53	18.38	6.55	0.69	9.13	3.03	0.32	4.52	10.85
C	50.57	20.89	9.50	0.50	1.87	3.63	0.10	5.65	6.76
Nepheline sienite	44.67	27.30*	4.10	—	1.50	0.68	15.70	5.65	0.40

\* Al<sub>2</sub>O<sub>3</sub> + TiO<sub>2</sub>.

TABLE 2

Clay	Granulometric composition of clays, %, by grain sizes, $\mu\text{m}$			
	> 50	50 – 20	20 – 2	< 2
A	31.3	7.3	11.3	50.1
B	25.0	3.2	28.7	43.1
C	47.2	14.2	16.4	22.2

For a long time these clays have been widely used in the production of porous ceramic articles such as structural and facing brick, roof tiles, glazed tiles for interior and exterior decoration of buildings, and pottery articles [1]. The application of these clays in the production of dense ceramic articles has been less thoroughly investigated [2]. The main reason for that is their narrow ( $\leq 60^\circ\text{C}$ ) sintering interval, which may cause deformation of the articles. This interval can be expanded by using several clay varieties which have different granulometric and mineralogical compositions or by introducing additives such as natural or synthetic wollastonite, nepheline sienite, etc.

The present investigation studied two ceramic mixtures (I and II) composed of three clay varieties, namely, two Quaternary deposits (clays A and B) and one Devonian deposit (clay C) with two kinds of fluxes: synthetic pseudowollastonite and nepheline sienite (Scheme 1). The chemical composition of mixtures I and II is (mass content, %) : 40 clay A, 40 clay B, and 10 clay C. 15% nepheline sienite was added to mixture I and 15% synthetic pseudowollastonite was added to mixture II. The chemical composition of the raw materials is given in Table 1. The pseudowollastonite was synthesized from lime containing 92.57%  $\text{CaCO}_3$  (with  $\text{MgO}$ ,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$  impurities) and sand containing 97.27%  $\text{SiO}_2$  (with  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{TiO}_2$ ,  $\text{Fe}_2\text{O}_3$  impurities) at a temperature of  $1450 - 1480^\circ\text{C}$ . A molar ratio  $\text{CaO} : \text{SiO}_2$  equal to 1 maintained in preparing the mixtures.

According to x-ray phase analysis data, the predominant crystalline phase in the synthesized glass crystalline material is actually pseudowollastonite (Fig. 1).

The granulometric composition of the clays determined on a Sedigraph-5100 automatic sedimentometer is given in Table 2.

The fluxes used (nepheline sienite and pseudowollastonite) have identical fusibility determined on an MN-2 heating microscope in the temperature interval of  $800 - 1250^\circ\text{C}$ . However, the fusibility of nepheline sienite begins to be manifested at a temperature that is  $100 - 120^\circ\text{C}$  lower than that of pseudowollastonite.

Mixtures and samples for the experiments were prepared according Scheme 2.

The main attention in the studies was paid to mixture sintering. This process was investigated using high-temperature differ-

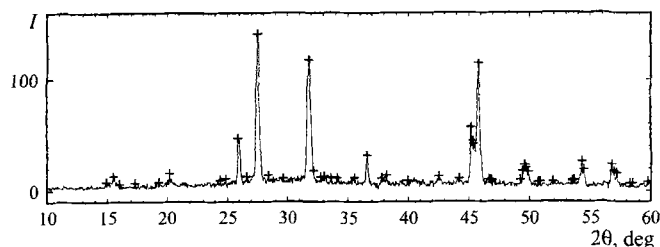
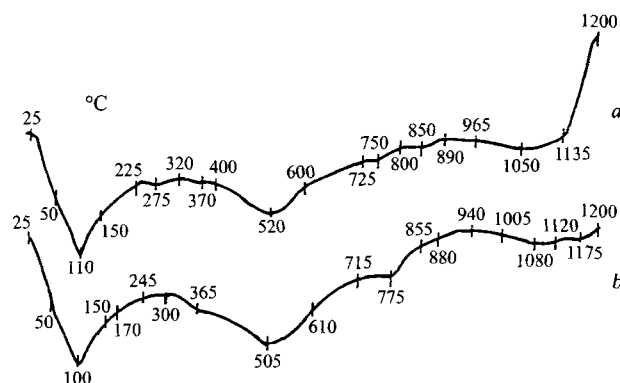
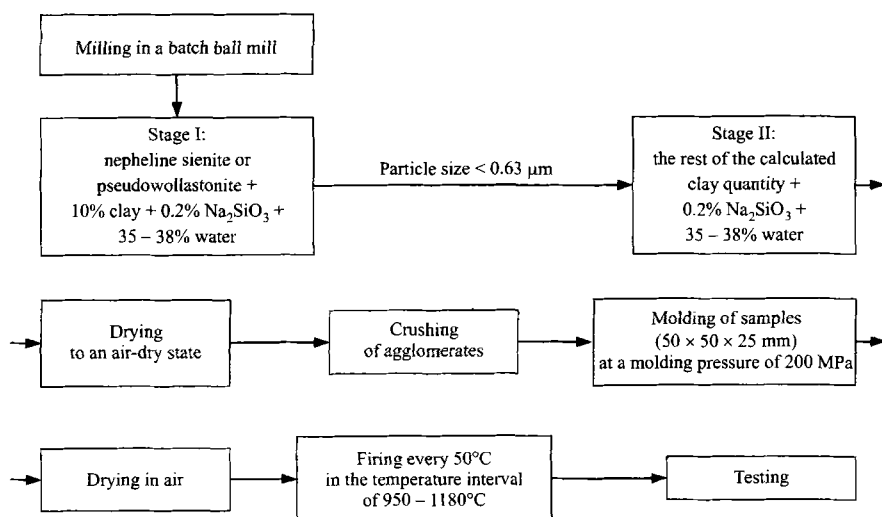
Fig. 1. X-ray pattern of synthetic pseudowollastonite (+ Ca,  $\text{FeSiO}_3$ ).

Fig. 2. DTA curves of mixtures I (a) and II (b).

ential thermal analysis, dilatometry, and x-ray phase analysis of samples fired every  $50^\circ\text{C}$  in the temperature interval of  $950 - 1150^\circ\text{C}$ .

The reactions occurring in mixtures I and II are determined primarily by the clay component.

The data obtained make it possible to evaluate the process of sintering mixtures I and II (Fig. 2) [2]. Adsorption water is removed in the temperature interval of  $110 - 150^\circ\text{C}$ , and at  $245 - 275^\circ\text{C}$  hydrated iron-bearing compounds such as goethite  $\alpha\text{-FeOOH}$  become dehydrated. Further processes at a temperature of  $300 - 320^\circ\text{C}$  are related to organic impu-



Scheme 2

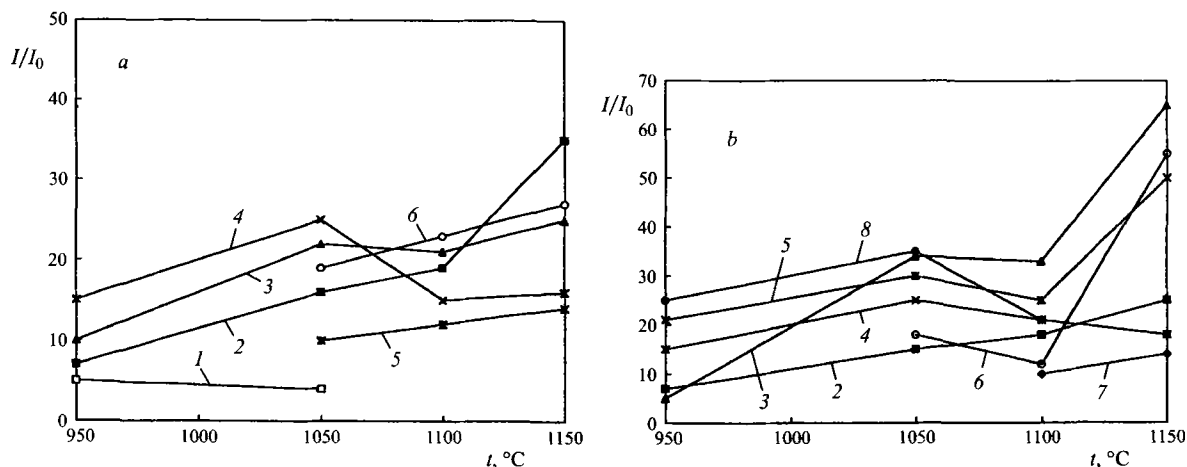


Fig. 3. Sequence of crystalline-phase formation in mixtures I (a) and II (b) in sintering: 1) nepheline; 2) hematite; 3) anorthite; 4) quartz; 5) gehlenite; 6) diopside; 7) cordierite; 8) wollastonite.

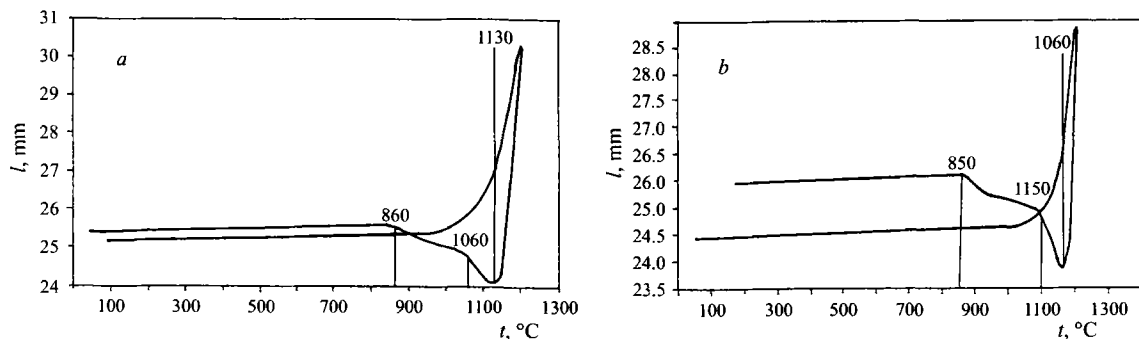


Fig. 4. Changes in linear shrinkage  $l$  in the course of sintering of mixtures I (a) and II (b).

rities burning out. Structural water is removed from the argillaceous materials at 505 – 520°C, and then at 1050 – 1080°C a liquid phase appears and formation of new crystalline phases begins (Fig. 3). The most significant differences in the crystalline-phase compositions are the formation of cordierite in mixture II and a higher degree of crystallization in the latter mixture, judging from the intensity of the crystalline phases.

As can be seen from the changes in shrinkage determined by laser dilatometry on cylindrical samples of height 35 mm and diameter 35 mm (Fig. 4), the process of sintering in mixtures I and II starts at temperatures of 850 and 860°C, respectively, and ends at 1110 – 1150°C. Judging from photomicrographs, the sintered material is crystalline with small fractions of a vitreous phase and pores. Channel-shaped pores prevail in ceramic material I, and rounded closed pores prevail in material II.

A minimum water absorption of  $\leq 2\%$  is reached in the temperature interval of 1070 – 1150°C, and the apparent density at this temperature is 1.91 – 2.40 g/cm<sup>3</sup>. The bending

strength of samples I and II fired at a temperature of 1080°C is 58 and 45 MPa, respectively.

Thus, based on three varieties of low-melting illite-containing clays with 15% additive of nepheline sienite or pseudowollastonite, a high-strength sintered (water absorption  $\leq 2\%$ ) ceramic material is formed in the temperature range of 1060 – 1150°C, and its sintering interval is sufficiently broad for mixtures I and II to be used in the production of household (lightly colored) articles and some types of building ceramics. In order to expand the sintering interval, it is advisable to use several varieties of clay of similar type.

## REFERENCES

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